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Abstract

ON THE BEHAVIOUR OF NITROSYLRUTHENIUM NITRATO COMPLEXES IN TBP-HNO_3 SYSTEM

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This work was undertaken to throw some light on the solvent extraction behaviour of the nitrato complexes of nitrosylruthenium in TBP-HNO_3 system. Both tracer (10^{-9}M) and macroscopic (10^{-3}M) concentrations of ruthenium have been investigated. For tracer work, the complexes were prepared by Martin's method while for macroscopic one, Fletcher's procedure was employed.

A comparative study of both preparates at 10^{-3}M Ru concentration, was undertaken spectrophotometrically. This has revealed, among other things, that Fletcher's procedure gives directly the nitrato complexes while Martin's method leads initially to RuO_4 in nitric acid which undergoes a series of successive reductions leading to the nitrato complexes after 17 hours. All tracer work was carried out after suitable aging time.

The extraction studies started with the system TBP-H_2O-HNO_3 without Ru and showed that the extractable species has the form TBP $(H_2O)_x$ HNO_3, where x was found to be equal to 1 and 4 depending on the method of evaluation, with more evidence in favour of 4. The equilibrium constant K for the formation of this product was calculated.

On the other hand, the extraction behaviour of nitrosylruthenium nitrato complexes at tracer and macroscopic concentrations was followed radiometrically. Measurements were carried out in equilibrium conditions. The results indicate the following:

(1) The variation of D_{Ru} with HNO_3 concentration has the same general feature for concentrations of TBP between 15 and 60% and for a very wide range of Ru concentrations (10^{-9} to 1.65×10^{-3}), irrespective of the method